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THE REDOX POTENTIAL OF BOROSILICATE GLASSES

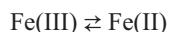
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The effect of different factors on the redox potential of potassium-borosilicate glasses is considered. It is demonstrated that this potential is formed under the effect of a number of opposite factors, where one of the factors often predominates. Thus, the raw materials have the deciding role in the formation of the redox potential of high-alkaline glasses. In predicting this potential, it is necessary to take into account the type and the coordination state of acid oxides.

The most common colorant impurity in clear glass is iron, whose bivalent ion decreases light transmission, impairs the color tint of glass, and decreases the diathermancy of the glass melt, which complicates the melting process, especially in continuous production [1]. Therefore, the content of ferric oxide (II) in construction and engineering glass should be stable, and in glass with enhanced light transmission it should be as low as possible.

Iron coexists in a glass melt simultaneously in two valence forms: Fe(II) and Fe(III). By controlling their ratio and shifting the state of equilibrium



it is possible to stabilize or decrease the FeO content to a required value.

The variation in the ratio of bivalent to trivalent iron is symbiotic to the value of the redox potential (ROP) of the glass melt, which is influenced by the glass composition, the raw materials, the temperature, the redox conditions of melting, and the total content of iron in glass [1].

The authors in [1] consider the effect of various factors on the modification of the ROP of soda-lime glass for construction and engineering purposes produced by the continuous production method. It is no less important to estimate the ROP in borosilicate glasses, since the $\text{R}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$ system is the basis for clear optical crowns that have to meet high requirements on light transmission in the visible spectrum range. Therefore, in melting optical glass it is important to use batch materials with a guaranteed low content of colorant impurities and to control the ROP of glass to ensure the maximum possible transition of the variable-balance elements (iron, copper chromium) into the non-tinting or weakly tinting forms.

The purpose of the present study was to analyze the ROP of alkaline-borosilicate glasses depending on the composi-

tion of glass, the melting temperature, and the type of raw materials used.

According to the method described in [1], an indicator showing the content of bivalent iron in glass was used for a quantitative evaluation of variations in the ROP of glass:

$$d_{\text{Fe(II)}} = (w_{\text{Fe(II)}} / w_{\text{Fe}_{\text{tot}}}) \times 100,$$

where $w_{\text{Fe(II)}}$ and $w_{\text{Fe}_{\text{tot}}}$ is the mass content, respectively, of bivalent iron and total (bivalent and trivalent) iron in glass converted to metal, %.

The content of Fe(II) in optical glass production is determined from the spectral curve of the iron absorption index [2]:

$$d_{\text{Fe(II)}} = - \frac{\log \tau_\lambda}{lw\rho\chi_{\lambda_{\text{Fe(II)}}}},$$

where τ_λ is the spectral coefficient of light transmission of the glass sample for the wavelength of 800 or 1000 nm, rel. units; l is the thickness of the glass sample, cm; w is the mass content of iron in glass converted to metal, %, determined by chemical analysis or by the spectrophotometric (OST 3-4728-89) methods; ρ is the density of glass, g/cm³; χ_λ is the volume absorption index of bivalent iron converted to a concentration of 10² g/cm³ of glass; for wavelengths of 800 and 1000 nm, $\chi_\lambda = 2.25$ and 3.6 cm²/g, respectively [2].

The glass compositions of the $\text{K}_2\text{O} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2$ system with 2% molar content of Al_2O_3 were selected in such a way as to have a constant content of B_2O_3 (series 1) or K_2O (series 2).

The glasses were synthesized from silicon dioxide, boric acid, and potassium nitrate and carbonate, all materials of the “extra pure” grade, and aluminum oxide of the “chemically pure” grade.

The amount of 0.3% Fe was added to all glass batches via Fe_2O_3 and 0.2% Al_2O_3 was also introduced in all batches.

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TABLE 1

Series	Molar content in glass, %			$d_{\text{Fe(II)}}$, %	n_D of glass	Part of $[\text{BO}_4]$, %	Melting temperature, °C
	K_2O	B_2O_3	SiO_2				
1	9.5	15.0	73.5	0.8	1.4945	35.3	1450
1	11.0	15.0	72.0	1.1	1.5008	51.0	1450
1	12.5	15.0	70.5	1.2	1.5025	52.0	1420
1	14.0	15.0	69.0	2.2	1.5105	73.0	1400
1	15.5	15.0	67.5	2.7	1.5117	73.0	1380
1, 2	17.0	15.0	66.0	4.3	1.5130	72.0	1350
1	23.0	15.0	60.0	10.6	1.5118	48.0	1350
2	17.0	18.8	62.2	2.4	1.5125	59.0	1360
2	17.0	10.7	70.3	4.8	1.5102	84.0	1370

Potassium oxide was simultaneously introduced via potassium nitrate (3% K_2O) and potassium carbonate (the remaining amount of K_2O) (here and elsewhere wt.%, unless otherwise specified).

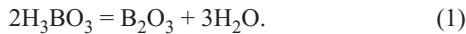
The glasses were melted in platinum crucibles of 100 cm³ in an electric laboratory furnace, and the melt was agitated by a platinum agitator. The glass melt was cast into graphite molds and annealed in a laboratory muffle. The cooled glass was used to make plane-parallel plates that served as sample in spectrophotometric measurements. The spectral transmission curves of the glasses were measured on a SF-26 spectrophotometer.

Table 1 lists the experimental glass compositions and some of their properties.

The ROP of the glasses of series 1 was influenced by the glass composition, the raw materials, and the melting temperature. Other terms were maintained constant, hence they can be neglected.

A decreased content of base oxides in glass and an increased content of acid oxides contribute to increasing the content of Fe(II), i.e., the reducing potential of glass [3]. The results in Table 1 contradict the general opinion, as the increase in the molar content of K_2O from 9.5 to 23% and a decrease in the molar content of $(\text{SiO}_2 + \text{B}_2\text{O}_3 + \text{Al}_2\text{O}_3)$ from 90.5 to 77% in series 1 glasses correlate with an increasing share of Fe(II) from 0.8 to 10.6%.

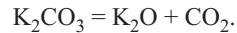
It is known that the relative content of ferric oxide (II) increases as the glass melting temperature grows [3]. However, a decrease in the melting temperature from 1450 to 1350°C in the considered compositions of series 1 (Table 1) was accompanied by increasing $d_{\text{Fe(II)}}$ from 0.8 to 10.6%, which contradicts the data in [3]. Consequently, the effect of raw materials on the ROP in glasses of series 1 is predominant due to the following fact. Silicon dioxide and aluminum oxide that are part of the experimental glass batch do not decompose in heating up to 2000°C [4]. Boric acid at a temperature over 185°C [4] loses water:



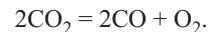
The literature has no data on the effect of water vapor on the content of Fe(II), i.e., on the ROP of glass. This fact can

be neglected for series 1 glasses, since the content of B_2O_3 in the system and, accordingly, the content of H_3BO_3 in the batch is constant. Consequently, an equal quantity of H_2O is released according to reaction (1) from all batches of series 1.

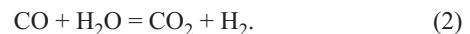
Potassium carbonate at the boiling temperature of 891°C decomposes:



The resulting carbon dioxide at a temperature of 1000°C completely dissociates into the reducing gas CO and oxygen [4]:



Carbon monoxide at a high temperature presumably reacts with the water vapor released by decomposing boric acid and forms hydrogen, which is a very intense reducing gas [4]:



Potassium carbonate in dissociation releases the gaseous product which, in our opinion, by itself or as a consequence of reaction (2), is capable of increasing the reducing potential of the batch and the glass, which ought to be accompanied by an increasing Fe(II) content in the glass.

The results of Table 1 corroborate this assumption: an increase in the content of K_2O mainly introduced via K_2CO_3 under a constant content of B_2O_3 introduced via boric acid into glass of series 1 correlate with a continuous increase of the content of bivalent iron from 0.8 to 10.6% and, consequently, with an increasing reducing potential of the glass.

Thus, an increase in the oxidizing potential in series 1 glass, which is related to an increasing K_2O content in glass and a decreasing melting temperature, is balanced by the more powerful reducing potential of the batch.

Figure 1 shows the part of Fe(II) in series 1 glass versus the content of K_2O and $(\text{SiO}_2 + \text{B}_2\text{O}_3 + \text{Al}_2\text{O}_3)$: this curve can be split into three rectilinear segments with a gradually increasing angle with the abscissa axis. The molar content of K_2O within the first segment grows from 9.5 to 12.5%, the Fe(II) part is virtually constant (0.8 – 1.2%), and the reducing potential in this case can be regarded as constant. Its variation Δ can be quantitatively estimated from the increase in the content of Fe(II), when the molar content of K_2O in glass changes by 1%:

$$\Delta\text{ROP} = \Delta d_{\text{Fe(II)}} / \Delta x_{\text{K}_2\text{O}}.$$

Within the first segment, $\Delta\text{ROP} = 0.13$. The oxidizing effect caused by the variations in the composition and the melting temperature in this stage is virtually balanced by the reducing effect of the batch.

The second segment (the molar content of K_2O in glass varies from 14 to 17%) is characterized by an accelerated

growth of the ferric oxide (II) content from 2.2 to 4.3% and, accordingly, the growth of the reducing potential of the batch: $\Delta\text{ROP} = 0.7$. The batch in this stage has a perceptible role and its reducing effect surpasses the opposite effect of the further growth of the K_2O content in glass and a decreased melting temperature.

Within the third segment (the molar content of K_2O increases from 17 to 23%) we observe the most intense growth of $d_{\text{Fe(II)}}$ from 4.3 to 10.6%. In this case, $\Delta\text{ROP} = 1.05$, i.e., the predominant reducing effect of the batch in the third stage is evident and quite significant and therefore it completely compensates the opposite effect caused by the variation of the glass composition and the melting temperature.

The K_2O content in the glasses of series 2 is constant and equal to 17%, and the SiO_2 content gradually increases at the expense of decreasing the B_2O_3 content (Table 1). The melting temperature varies insignificantly and its effect on the ROP of glass can be neglected. In our opinion, the effect of the batch of the glass ROP in this series can be neglected as well, since the K_2O content is constant and, consequently, the content of potassium carbonate in the batch is constant.

Accordingly the fluctuations of the Fe(II) content registered in series 2 glasses are a function of the variation of the composition.

It follows from the data in Table 1 that the content of K_2O in series 2 glasses is constant and the molar content of acid oxides ($\text{SiO}_2 + \text{B}_2\text{O}_3 + \text{Al}_2\text{O}_3$) does not vary either and amounts to 83%. At the same time, the content of Fe(II) becomes 2 times higher: from 2.4 to 4.8%. Hence, it is evident that the type of the acid oxide as well has a significant effect on the ROP of glass.

It is known that oxides integrating glasses of series 1 and 2 depending on their increasing acid properties are ranked as follows:

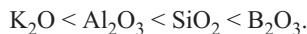


Figure 2 shows the variations of $d_{\text{Fe(II)}}$ in series 2 glasses depending on the molar content of B_2O_3 . It can be seen that an increase in the B_2O_3 content correlates with a decreasing Fe(II) content, i.e., boric anhydride increases the oxidizing potential of glass, which contradicts the data in [5].

The studies of glasses of the $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$ system [6] made it possible to refine the above sequence taking into account the coordination state of boron in glass:



i.e., in predicting variations of the ROP, it is necessary to take into account the coordination state of boric anhydride. To estimate the content of four-coordination boric anhydride in glasses, the refractive indexes were calculated according to the method proposed by L. I. Demkina, and the deviation of the measured values from the estimated ones gave the needed value [7].

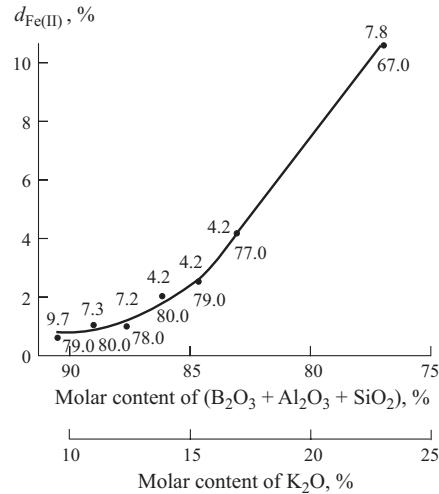


Fig. 1. Fe(II) content versus the component content in series 1 glasses. Figures above the curve show the absolute molar content of $[\text{BO}_3]$, and figures below the curve indicate the molar content of $(\text{SiO}_2 + [\text{BO}_4])$.

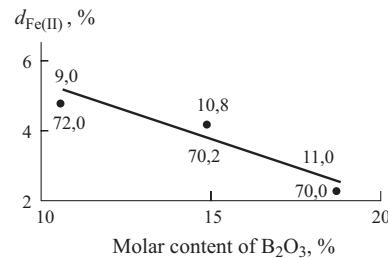


Fig. 2. Fe(II) content versus the B_2O_3 content in series 2 glasses. Figures above the curve show the absolute molar content of boric anhydride in the form of $[\text{BO}_4]$, and figures below the curve indicate the total molar content of $(\text{SiO}_2 + [\text{BO}_3])$.

It can be seen in Fig. 2 that as the molar content of $[\text{BO}_4]$ increases and the content of $(\text{SiO}_2 + [\text{BO}_3])$ decreases, the content of Fe(II) becomes lower, i.e., the reducing potential of the glass drops. This corroborates the conclusions made in [6] regarding lower acidity of $[\text{BO}_4]$ compared with that of SiO_2 and $[\text{BO}_3]$.

A need to take into account the coordination state of boron in estimating the ROP follows from Fig. 1. Within the variation interval of the K_2O molar content from 14 to 23%, the Fe(II) share grows perceptibly from 2.7 to 10.6%. This correlates with the constantly growing content of the most acid component $[\text{BO}_3]$ and the decreasing quantity of the less acid oxides $(\text{SiO}_2 + [\text{BO}_4])$.

Thus, the ROP of potassium-borosilicate glasses is a superimposition of the effects of the composition, the melting temperature, and the type of raw materials. The batch has the predominant effect on the formation of the ROP in highly alkaline glasses. The effect of acid oxides on the ROP of borosilicate glass correlates with the type and the coordination state of these components.

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